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Integrated working fluid-thermodynamic cycle design of organic Rankine cycle power systems for waste heat recovery

Stefano Cignitti^a, Jesper G. Andreasen^b, Fredrik Haglind^b, John M. Woodley^a, Jens Abildskov^a

^a*Process and Systems Engineering Center (PROSYS), Department of Chemical and Biochemical Engineering, Technical University of Denmark, Building 229, 2800 Kgs. Lyngby, Denmark*

^b*Department of Mechanical Engineering, Technical University of Denmark, Building 403, 2800 Kgs. Lyngby, Denmark*

Abstract

Today, some established working fluids are being phased out due to new international regulations on the use of environmentally harmful substances. With an ever-increasing cost to resources, industry wants to converge on improved sustainability through resource recovery, and in particular waste heat recovery. In this paper, an organic Rankine cycle process and its pure working fluid are designed simultaneously for waste heat recovery of the exhaust gas from a marine diesel engine. This approach can overcome design issues caused by the high sensitivity between the fluid and cycle design variables and otherwise high resource demands, which through conventional methods cannot be addressed. The global optimal design was a 1.2 MW cycle with 2,2,3,3,4,4,5,5-octafluorohexane as the new fluid. The fluid has no ozone depletion potential and a global warming potential under the regulatory limit. By using the simultaneous design approach the optimum solution was found in 5.04 seconds, while a decomposed approach found the same solution in 5.77 hours. However, the decomposed approach provided insights on the correlation between the fluid and cycle design variables by analyzing all possible solutions. It was shown that the high sensitivity between the fluid and cycle design variables was overcome by using the simultaneous approach. Correlation between net power output and the product of the overall heat transfer coefficient and the heat transfer area could further be addressed by employing a new solution strategy including maximum constraints for this product. The use of such constraints resulted in the design of a new fluid (5-chloro-4,5,5-trifluoro-2,3-dimethylpent-2-ene) with a 1.25 MW net power output. Finally, a comparison with conventional fluids was shown where 2,2,3,3,4,4,5,5-octafluorohexane offered an improvement on net power output and economic and environmental metrics.

Keywords: *Integrated design; optimization; CAMD; organic Rankine cycle; working fluid; waste heat;*

Nomenclature

<i>Symbol</i>		<i>Superscript</i>	
A	Heat transfer area (m ²)	U	Upper bound
C_{p,A}	Ideal gas heat capacity parameter	L	Lower bound
C_{p,B}	Ideal gas heat capacity parameter	<i>Subscript</i>	
C_{p,C}	Ideal gas heat capacity parameter	g	Exhaust gas
C_{p,D}	Ideal gas heat capacity parameter	i_l	Group set
C_{p,ig}	Ideal gas heat capacity (J/mol/K)	LMTD	Logarithmic mean temperature difference
F_r	Flow rate working fluid (mol/h)	ph	Phase set
GWP	Global warming potential (CO ₂ eq)	s	Isentropic process
h	Enthalpy (J/mol)	st	Stream/stage set
n	Number of group	w	Cooling sea water
ODP	Ozone depletion potential (R11eq)		
P	Pressure (bar)		
P_c	Critical pressure (bar)		
q	Molecular structure type		
s	Entropy (J/mol/K)		
T	Temperature (K)		
T_c	Critical temperature (K)		
U	Overall heat transfer coefficient (W/m ² /K)		
v	Valency		
W_{net}	Net power output (J/h)		
Z	Compressibility		
φ	Fugacity coefficient		
Ψ, Ω	Equation of state parameter		
ω	Acentric factor		

1. Introduction

Recovering waste heat from processes requires significant effort in the design and optimization of the working fluid as well as the thermodynamic cycle. Environmental regulations have been a driving force for the industry to seek novel working fluids since many conventional fluids are being phased out. This follows the Kyoto Protocol in 1997 and more recently new EU regulations from 2014 [1,2], which restrict the use of some working fluids currently in use [3]. However, design of a new working fluid poses a challenge and finding an optimum solution for a given application often results in a trade-off between cycle performance, and environmental and safety criteria. Furthermore, low-temperature (low-grade) waste heat sources pose additional challenges to make the recovery technically and economically feasible [4–6]. Amongst others, hydrofluoroolefins (HFOs) have been suggested as a potential future class of low global warming potential working fluids. However, data for such fluids is scarce in conventional databases [7–10]. These issues have led to the development of several methods and tools for designing new working fluids and organic Rankine cycle (ORC) power systems.

Most of these methods are based on computer-aided molecular design techniques (CAMD) to design alternative or novel working fluids [11]. Papadopoulos et al. (2012, 2010a, 2010b) proposed a systematic design approach for working fluid generation for ORC units. Here, a weighted objective function based on scaled pure properties was proposed and used. As reported in their work, ten pure fluid properties are influential in the cycle performance and in the feasibility of the solution. Specifically, three of these process metrics are important to optimize. Initially [12], the authors used the weighted objective function employing all of the important pure fluid properties. Subsequently, the problem was reformulated into a multi-objective optimization problem considering only five of the pure fluid properties [13]. Finally, the cycle performance was evaluated for one or more solutions. Palma-Flores et al. (2015) also proposed a method for choosing the optimal pure working fluid for an ORC unit using a CAMD approach. The objective function here was based on temperature dependent pure fluid properties.

Other authors have taken approaches which avoid CAMD method and start either with a set of chosen fluids or apply a reverse engineering approach. For example, Andreasen et al. (2014) proposed a methodology for working fluid selection for an ORC unit for use of low-temperature heat. Thirty pure and mixed working fluids were selected through optimization of the ORC unit. The fluids were ranked according to the objective function, which was the cycle net power output. Likewise a reversed engineering approach can be employed, where the optimal fluid properties are found through an optimization problem without regard to chemical feasibility or stability of the molecule. Molecules that then match these properties are found in a subsequent step. Such methods have been reported in several works and frequently such a solution approach has been found necessary due to the complexity of the thermodynamic model employed [17–19]. These methods are usually termed a continuous-molecular targeting approach (CoMT-CAMD). The works presented tend to optimize all the fluid properties, which is a difficult task, given the correlation between properties that may make the result in local optima [5,20]. The issue of correlated properties also holds true when considering the detailed design of certain components in the ORC unit that cannot solely be based on primary fluid properties [21].

The current state-of-the-art offers methods for designing fluids for organic Rankine cycle units from a sequential (or decomposed) approach, where the working fluid design and process optimization are carried out in separate steps. This results in sub-optimal solutions on account of high correlation between fluid and process variables. In this way, the methods are not able to obtain a global optimal design of working fluid and process.

In contrast, in the work we report here, for the first time, a simultaneous approach is proposed for integrated pure working fluid and process design for organic Rankine cycle power systems. We reasoned that such an approach would have the benefit of : i) a pre-screening step to avoid a sub-optimal starting point, ii) the design of alternative or new fluids that are environmentally friendly and have similar or improved cycle performance compared to conventional fluids, iii) a rapid search for the global optimum. The approach is based on the use of CAMD, property prediction and mathematical programming techniques to define the fluid-process targets and models, which are combined and solved simultaneously. Additionally we have included for the first time the design of bicyclic and branched cyclic molecules using CAMD.

This paper will first present the problem description, followed by the approach used and the models needed. Subsequently, the results for the simultaneous design strategy are presented and compared to a decomposed design strategy. The discussion section focusses on the sensitivity of the design variables, the advantage of the simultaneous approach, and on whether the global optimum is found. Finally, the novel fluid resulting from the optimization is compared to conventional fluids.

2. Methods

The integrated method employed in this work is summarized in the workflow shown in Figure 1. Several methods were used to simultaneously design alternative or novel working fluids for the organic Rankine cycle process. CAMD was used to enable a model-based description as reported previously (Cignitti et al. (2015) and Zhang et al. (2015)). Meanwhile, the cycle itself was described through classical mass and energy balances. Fluid properties (enthalpy (h), entropy (s) and fugacity (ϕ)), were predicted using the Soave-Redlich-Kwong (SRK) equation of state (EoS) [23].

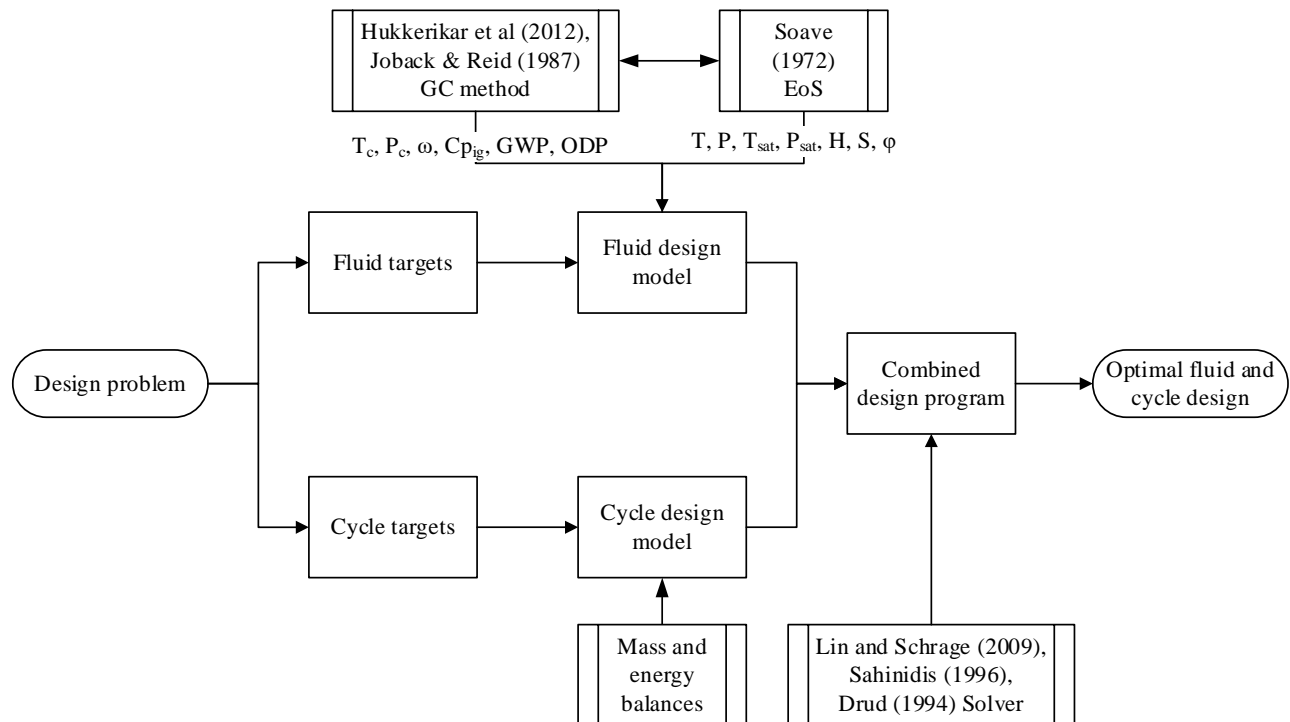


Figure 1: Integrated design workflow

The pure fluid properties were predicted by group contribution (GC) methods that calculate the properties from the molecular structure of the working fluids. For this, the method of Hukkerikar et al. (2012) was used to predict critical properties and the acentric factor. The method of Joback and Reid (1987) was used to predict the ideal gas heat capacity. Finally, the method of Hukkerikar et al. (2012) was used to calculate any missing group contributions for some groups and for the prediction of global warming potential (GWP) and ozone depletion potential (ODP). The GWP and ODP give a good indication whether or not the fluid complies with refrigerant regulations [2].

The fluid and process design methods were applied to the design of an ORC unit which was proposed for waste heat recovery from internal combustion engines, [26–28]. In the case studied here the waste heat originated from a 37 MW marine diesel engine (model: 7G95ME-C9.5 with LP SCR & EGB tuning [29]) from MAN Diesel & Turbo. Marine diesel engines produced significant amount of waste heat from exhaust gasses which can potentially be recovered for electricity generation. The resulting electricity could meet the electricity demand on the ship, cooling of ship containers or reducing the shaft work for propelling the ship. In all cases, the result would be a significant reduction in fuel consumption by reducing the load on main or auxiliary engines.

To match the cycle, a fluid also needs to be selected. The fluid should enable a high production of electricity and respect environmental and safety regulations. On this premise it was decided to search for acyclic, alicyclic and aromatic hydrocarbons that contain double bonds, fluorine and maximum one chlorine atom if fluorine and double bonds were present. This ensures that the designed fluid has a low global warming potential and ozone depletion potential.. The selection was based on common fluids utilized in such cycles [16] and on guidelines from regulations [2,3].

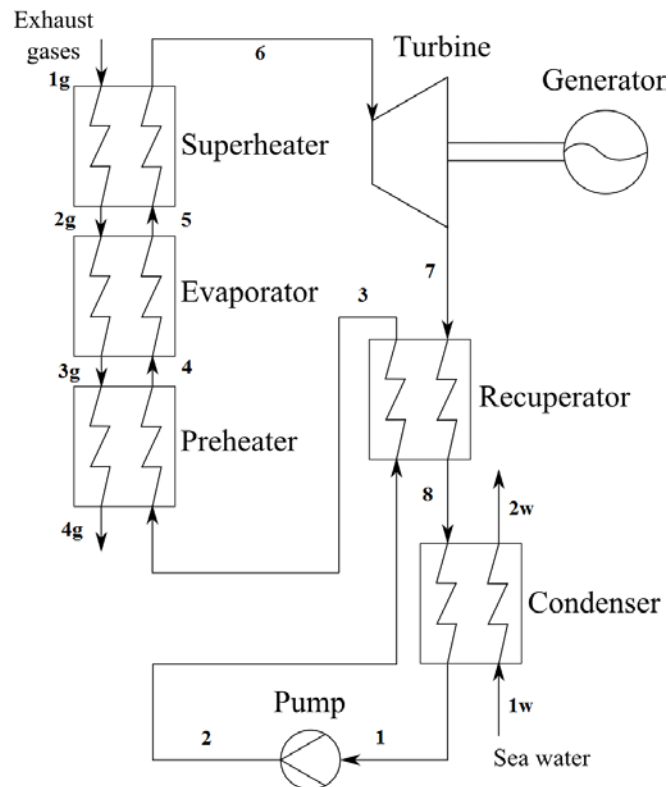


Figure 2: Flowsheet of the ORC unit with recuperator.

A flowsheet of the ORC system is given in Figure 2. The ORC unit contains a turbine, recuperator, condenser, pump and boiler. Here, the boiler is divided into three sections: preheater, evaporator and super-heater. A configuration with a recuperator was chosen such that the feed temperature of working fluid to the boiler is high. The modeling conditions used for the ORC unit are provided in Table 1. The design of the ORC unit was considered at the 75 % load point of the diesel engine. The mass flow rate and the temperature of the exhaust gases were obtained from the CEAS engine calculation tool [29]. In order to accommodate on-board heating demands, for example fuel preheating, fuel tank heating and space heating, the exhaust gases were used to generate 2000 kg/h of service steam at 7 bar prior to entering the ORC unit boiler. In this way, the temperature of the exhaust gas was reduced by around 21 K. The exhaust gas temperature denoted in Table 1 is the temperature after the service steam boiler. The values indicate that 35 MW of heat was contained in the exhaust gas given the assumption of constant heat capacity. The efficiencies (η) for the pump and turbine are isentropic efficiencies. The seawater temperatures were fixed at 294 K at the inlet and 299 K at the outlet.

Table 1: ORC process operation and parameters

Parameter	Value	Unit
T_{1g}	509	K
C_{pg}	31.86	J/mol.K
F_g	2161.15	mol/s
T_{1w}	294	K
T_{2w}	299	K
η_{pump}	0.7	-
η_{turbine}	0.8	-

From the problem statement, the fluid and cycle targets were defined.

2.1 Fluid targets

Based on an analysis of working fluid databases [7,30] the following target properties were chosen, summarized in Table 2. The bounds for critical temperature (T_c), critical pressure (P_c) and acentric factor (ω) are large in order not to restrict the search space,. Previous studies suggest that it is not possible to restrict the search space by confining the values of these three properties, let alone the value of ideal gas heat capacity ($C_{p,ig}$), since a global sensitivity analysis indicates no clear relationship between these properties and the ORC unit performance [31]. This was then a further argument for employing a CAMD method rather than a database search method, because it would require a combinatorial evaluation of all possible database entries. For the same reason, $C_{p,ig}$ was not bounded, and Global Warming Potential (GWP) and Ozone Depletion Potential (ODP) are inherently addressed at the product type selection, however. All three properties were kept as constitutive variables and models were therefore required for their calculation.

Table 2: Target molecular properties

Property	Lower bound	Upper bound	Unit
T_c	368	600	K
P_c	18	100	Bar
ω	0	1	-
$C_{p,ig}$	-	-	J/mol.K
ODP	0	-	eqR11
GWP	0	-	eqCO ₂
Structure			

n	3	9	-
n_{i1}	0	9	
n_{branch}	0	9	
q	-1	1	

2.2 Cycle targets

In order to ensure feasible cycle results, the process variable specifications shown in Table 3 were selected. It was assumed that the sulfur content in the fuel was 3 % (by weight) giving a sulfuric acid dew point of 135 °C [32]. The lower bound for the boiler feed temperature was therefore selected as ($T_3 = 408$ K) to ensure that the minimum temperature in the exhaust gas boiler was always above the sulfuric acid dew point. By employing a high lower bound for the boiler feed temperature, it was necessary to recover a significant amount of heat in the recuperator. This was only possible for a few conventional fluids with very dry characteristics such as Hexamethyldisiloxane (MM) [33]. Seawater was used as the cooling fluid in the condenser.

Table 3: ORC unit specifications

Variable	Lower bound	Upper bound	Fixed Value	Unit
$\Delta T_{6,5}$	10	50		K
ΔT_{boiler}	20			K
$\Delta T_{\text{recuperator}}$	10			K
ΔT_{water}			5	K
T_1	300			K
T_3	408			K
P_1	0.05			bar
P_2		80% of P_c		bar

Furthermore, pressure losses were neglected in the ORC process.

2.3 Molecular working fluid model

The CAMD model uses a set of constraints that describe chemically feasible molecules in combination with GC property prediction functions. Among 220 first order groups available from Hukkerikar et al. (2012) the following groups were selected: CH₃, CH₂, CH, C, CH₂=CH, CH=CH, CH₂=C, CH=C, C=C, CF₃, CF₂, CF, CH₂F, CHF, CHF₂, HCClF, CCIF₂, CH₂(cyc), CH(cyc), C(cyc), CH=CH(cyc), CH=C(cyc), C=C(cyc), CH₂=C(cyc), CF₂cyc, CFcyc, aCH, aC, aC-CH₂, aC-CH, aC-CH₃, aC-C, aC-CH=CH₂, aC-CH=CH, aC-C=CH₂ and aC-F. Through classification of the different structural groups based on their valencies, the octet rule (Eq. 1) provides a simple relation for the structural feasibility of a given collection of groups [34]:

$$\sum_{i_2 \in G_1} (2 - v_{i_1}) n_{i_1} = 2q \quad (1)$$

$$\sum_{i_1 \neq i_2, i_1, i_2 \in G_1} n_{i_2} \geq n_{i_1} (v_{i_1} - 2) + 2 \quad \forall i_1, i_2 \in G_1 \quad (2)$$

Eq. (2) ensures single bonds between groups. The parameter $n_i^{(1)}$ is the number of first-order groups G_i of set i in the target molecule, v_i the valency of group i and q is assigned the value of 1, 0 or -1 for acyclic, monocyclic

or bicyclic groups, respectively. Bicyclic groups require additional constraints. Additional constraints were placed on the number ($n_i^{(1)}$) of groups to keep it within lower and upper bounds, n_i^L and n_i^U , respectively:

$$n_i^L \leq n_i \leq n_i^U \quad (3)$$

A further constraint was placed on the total number of groups making up a given molecule:

$$n^L \leq \sum_{i_1 \in G_1} n_{i_1} \leq n^U \quad (4)$$

Eqs. (1)-(4) are valid for structural combination of first order molecular groups. However, these equations are only sufficient to describe acyclic molecules or monocyclic molecules with no branches. Thus, additional equations for this work were required. They were defined to allow for bicyclic and branched cyclic molecules with and without side branches. An equation was defined for structural constraints of alicyclic groups for monocyclic and bicyclic type:

$$n^L \leq \sum_{i_1 \in G_{Alicyclic}} n_{i_1} \leq (n^U - (n^U - 2)q) \quad (5)$$

$$-2q \leq n_{CH_{(cyc)}} \quad (6)$$

Similarly, equations were defined for aromatic monocyclic and bicyclic molecules:

$$\sum_{i_1 \in G_{Aromatic}} n_{i_1} = 6 - 4q \quad (7)$$

$$-2q \leq n_{aC} \quad (8)$$

Further, an additional equation was defined for the number of branched chains on the cyclic molecule:

$$\sum_{i_1 \in G_{Acyclic}} n_{i_1} \leq n_{branch}^U \left(\sum_{i_1 \in \{G_{Alicyclic}, G_{Aromatic} | v_{i_1} \geq 3\}} n_{i_1} (v_{i_1} - 2) + 2q \right) \quad (9)$$

To ensure at least one fluorine and a double bond was present when a molecule with chlorine was designed, the following constraints were also included:

$$\begin{aligned} Y_{Cl} &= \sum_{i_1 \in G_{Chlorine}} n_{i_1} \\ Y_{Cl} &\leq \sum_{i_1 \in G_{Fluorine}} n_{i_1} \\ Y_{Cl} &\leq \sum_{i_1 \in G_{DoubleBonds}} n_{i_1} \\ Y_{Cl} &\in \{0, 1\} \end{aligned} \quad (10)$$

The SRK EoS equation was utilized [23,35]. Its equations were provided in the supplementary material, Eqs. (7)-(12).

2.4 ORC unit model

The target for the process is to maximize the net power output, which is the difference between the turbine power and pump power:

$$\dot{W}_{net} = \dot{W}_{Turbine} - \dot{W}_{pump} \quad (11)$$

This can be reformulated into an expression based on working fluid enthalpies:

$$\max \dot{W}_{net} = F_r \left((h_{6,2} - h_{7,2}) - (h_{2,1} - h_{1,1}) \right) \quad (12)$$

The remaining equations for the ORC unit model are given in the supplementary material. Energy balances over the heat exchangers were defined for flow rate and UA calculation. The general equations used for the UA calculations (Eq. 14 and 15) were complemented by the equations given in the supplementary material:

$$UA = \frac{\dot{Q}}{LMTD} = \frac{F(h_{in} - h_{out})}{LMTD} \quad (13)$$

$$UA_{boiler} = UA_{preheater} + UA_{evaporator} + UA_{superheater} \quad (14)$$

2.5 Mixed-integer nonlinear program for integrated design

Out of the molecular groups selected for design, six group contributions were missing for T_c , P_c and ω . The missing group contributions were calculated using the GC+ method and are provided in Table 4 using data from Hukkerikar et al. (2012).

Table 4: Estimated group contributions for missing groups using [24] method

Group i_I	T_{ciI}	P_{ciI}	ω_{iI}
CCl₂	5.85	0.03	0.08
CF	0.89	0.02	0.05
HCCIF	3.49	0.04	
C=C_(cyc)	2.35	0.01	
CF_{2cyc}	1.4		
CF_{cyc}	1.3	0.02	

The resulting mathematical program is a mixed-integer nonlinear program (MINLP). The model has 85 variables (21 discrete) and 132 constraints with 1112 Jacobian elements, 396 of which were nonlinear. The Hessian of the Lagrangian has 57 diagonal elements, 360 elements below the diagonal, and 67 nonlinear variables.

2.6 Software

The solution to the MINLP requires selection of a solution strategy and solver. LINDOGlobal was selected as the MINLP solver for the simultaneous solution strategy, being a global optimal solver that was documented

to find global optimal solution even for possibly non-convex problems [36]. The software used was GAMS [37], into which the MINLP was implemented.

3. Results and discussion

The solution of the MINLP containing the fluid design model and cycle model is summarized in Table 5. The solutions obtained were in three parts; first the program solved for acyclic molecules, then alicyclic molecules and finally aromatic molecules. The results suggest that the optimal solution for an acyclic molecule is a hydrofluorocarbon giving 1.21 MW of net power output. The acyclic and aromatic solutions have slightly lower objective function values of 1.20 MW and 1.05 MW, respectively. The two cyclic compounds require sub-atmospheric pressure conditions in the condenser, although they require similar operational conditions in the cycle compared to the acyclic solution. The acyclic solution gives excellent environmental properties with a zero ODP and very low GWP value. To the best of our knowledge, the acyclic fluid is not available in any commercial or in-house databases. However, the synthesis could be performed from a hexane backbone or a double deoxygenation reaction of 2,2,3,3,4,4,5,5-Octafluoro-1,6-hexanediol, which is a common fluid (National Center for Biotechnology Information). The other two designed fluids are novel as well. In an industrial setting, these fluids need to be synthesized and then subsequently analyzed to obtain experimental properties before being tested in a pilot and full-scale organic Rankine cycle process.

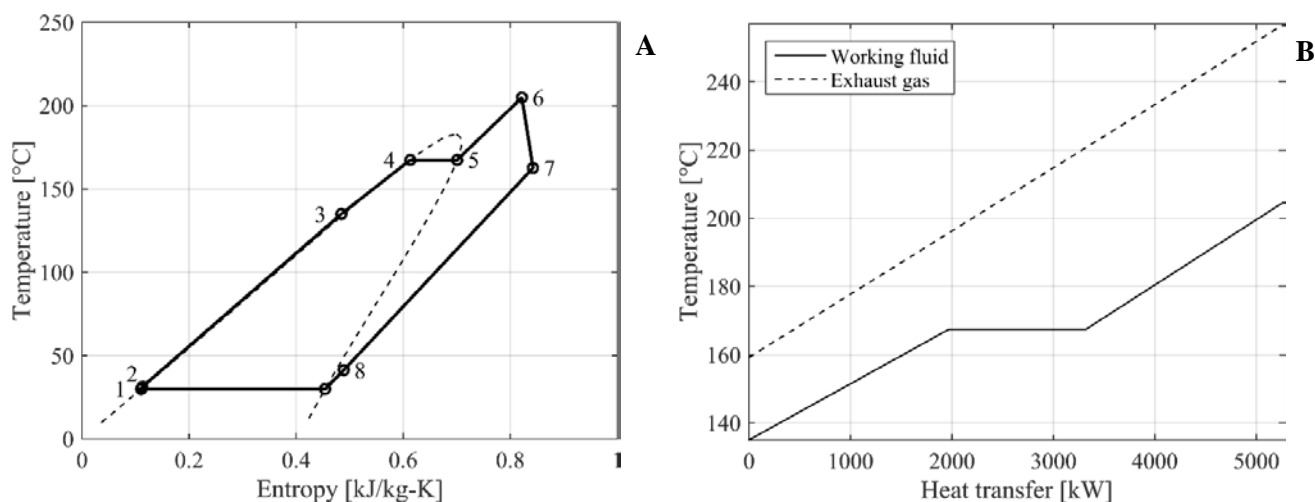
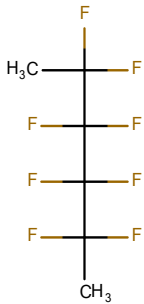
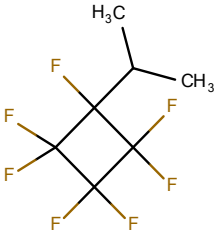
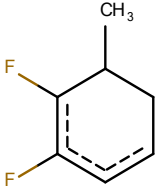


Figure 3: Diagrams for optimal acyclic solution. T-S diagram (A) and Q-T diagram (B).

Figure 3 (A) T-S-diagram for the ORC unit. The number on the diagram indicates the stages in the cycle. In Figure 3 (B) Q-T diagram for the boiler.

Table 5: Simultaneous optimization results with pinch-point constraints

Variable	Acyclic	Alicyclic	Aromatic
Structure			
n_1	2 CH ₃ ; 4 CF ₂	2 CH ₃ ; 1 CH; 3 CF ₂ cyc; 1 CFcyc	3 aCH; 1 aC-CH ₃ ; 2 aC-F
IUPAC	2,2,3,3,4,4,5,5-octafluorohexane	1,1,2,2,3,3,4-heptafluoro-4-(propan-2-yl)cyclobutane	1,2-difluoro-6-methylcyclohexa-1,3-diene
q	1	0	0
\dot{W}_{net} (W)	1,205,257	1,198,266	1,052,569
T_c (K)	455.83	451.16	588.39
P_c (bar)	30.69	24.45	36.84
ω	0.20	0.32	0.32
GWP (CO ₂ eq)	5.88	_*	_*
ODP (R11eq)	0	_*	_*
$C_{p,A}$	-5E+01	-2E+02	-3E+02
$C_{p,B}$	1E+00	2E+00	2E+00
$C_{p,C}$	-1E-03	-3E-03	-3E-03
$C_{p,D}$	4E-07	1E-06	2E-06
P_1 (bar)	1.17	0.75	0.05
P_2 (bar)	24.55	19.56	2.49
T_1 (K)	303.15	303.15	311.75
T_2 (K)	304.42	304.42	311.87
T_3 (K)	408.15	408.15	408.15
T_4 (K)	440.60	437.23	426.28
T_6 (K)	478.04	485.16	476.28
T_7 (K)	435.84	440.50	434.18
T_8 (K)	314.42	314.42	321.87
T_{g1} (K)	509.00	509.00	509.00
T_{g2} (K)	480.47	476.50	489.93
T_{g3} (K)	460.60	457.23	446.28
T_{g4} (K)	432.37	433.26	438.77
F_r (mol/s)	154.12	138.11	91.60
UA_{boiler} (W/K)	191,453	192,338	128,689
$UA_{\text{condenser}}$ (W/K)	343,236.12	338,722.77	188,646.89
$UA_{\text{recuperator}}$ (W/K)	270,268.20	225,186.86	133,944.95
* Property cannot be predicted with given groups			

3.1 Decomposed approach

For analysis of all the results, a decomposed solution approach was used. Here, the the fluid mixed-integer linear program (MILP) problem is solved independently and subsequently each solution is fed to the cycle (nonlinear program (NLP)). For the decomposed solution approach, the BARON solver was used for the MILP [39] and CONOPT solver for the NLP [40]. A decomposed solution strategy was then applied The first problem is an MILP that contains the molecular structure constraints and property prediction constraints with the product-related targets (Eqs. (1)-(10) and Eqs. (1)-(18) in the supplementary material). For each solution, an NLP program was solved containing the remaining equations of the program (Eqs. (12)-(15) and Eqs. (19)-(58) in the supplementary material). The result is that in total 9124 candidates were identified, of which 2062 fluids were found feasible for the ORC The ten best results are given in Table 6. The results have been summarized only and the full list of results is provided in the supplementary material.

Table 6: Decomposed solution strategy using pinch-point optimization

Solution	\dot{W}_{net} (W)	T_c (K)	P_c (bar)	ω	P_1 (bar)	P_2 (bar)	T_1 (K)	T_6 (K)	T_{g4} (K)	F_r (mol/s)
acyclic3588	1,205,256	455.83	30.69	0.203	1.17	24.55	303.15	478.04	432.37	154.11
acyclic6209	1,171,494	597.66	95.61	0.126	0.23	6.52	303.15	464.00	430.74	121.65
acyclic6207	1,170,371	597.22	91.38	0.142	0.20	6.22	303.15	465.36	431.44	118.10
acyclic4600	1,170,320	599.44	43.88	0.183	0.07	2.58	303.15	464.68	431.06	112.40
acyclic4600	1,170,320	599.44	43.88	0.183	0.07	2.58	303.15	464.68	431.06	112.40
acyclic4262	1,169,981	594.00	99.80	0.114	0.28	7.03	303.15	461.56	429.56	126.64
acyclic4262	1,169,960	594.00	99.80	0.114	0.28	7.03	303.15	461.57	429.56	126.63
acyclic4467	1,169,125	598.73	42.19	0.206	0.06	2.35	303.15	464.28	430.84	109.86
acyclic6426	1,168,849	591.98	41.16	0.205	0.07	2.59	303.15	464.82	431.08	111.28
acyclic6067	1,168,368	586.30	90.68	0.136	0.26	6.84	303.15	461.81	429.64	125.08

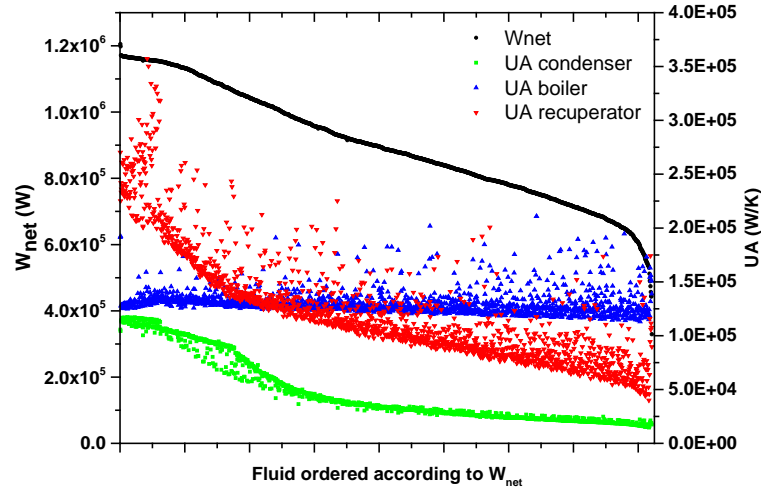


Figure 4: Decomposition results for \dot{W}_{net} optimization and resulting UA values. The results are ordered on the x-axis from fluid with highest \dot{W}_{net} to the fluid with the lowest \dot{W}_{net} .

As expected, the highest net power output is achieved by an acyclic fluid and this matches the solution from the simultaneous solution approach. Figure 4 shows the entire spectrum of the objective function plotted against UA values for the heat exchangers. The figure indicated little correlation between the ORC performance and UA boiler size. However, a clear relation is seen with the condenser and recuperator UA values.

The case study clearly demonstrates the successful application of the integrated approach. Additionally, the decomposition data suggest that the best result matches the simultaneous approach and finds all possible solutions, although at the expense of extra resources. In the following section, the simultaneous and decomposed approach will be compared. The correlation between product properties and process variables will be discussed to support the decision made with respect to the simultaneous approach that has been proposed. Finally, an alternative optimization strategy will be presented, given the arguments on the issue with sensitivity between \dot{W}_{net} and UA-values.

3.2 Comparison with conventional approaches

The decomposed approach represents a conventional approach where, given a set of heuristic criteria, a set of feasible fluids are generated or selected. Subsequently, each fluid may be tested, designed and optimized in the cycle [15,41].

3.2.1 Decomposed approach

The simultaneous solution approach solved the entire MINLP simultaneously. The decomposed solution solved the product MILP and a subset of process NLP for each candidate fluid. This results in an equal separation of blocks of equations as given in Table 7. In addition, continuous and discrete variables are given separately. Cumulatively, the number of variables in the MILP and NLP are larger than in the simultaneous MINLP due to the number of common variables. Product properties that are not constrained are calculated in post-phase as described in Table 7. The difference in number of equations and variables is not necessarily negative, although it is clear that the resources required are significantly different (See Table 1 in the supplementary material). The time for solving the MINLP is 5.04 seconds. However, the solution time for finding all the 9124 fluid candidates is 5760 seconds (1.60 hours) and the resulting computation time for solving the NLP for all the ORC unit is 15002 seconds (4.18 hours). Thus, the total time for solving the decomposition problem is 20762 seconds (5.78 hours). The simultaneous solution is therefore the least computationally expensive.

Table 7: Resources and program information for simultaneous and decomposed solution approach

Metric	Simultaneous MINLP	Product MILP	Post-calculation of each fluid	Process NLP
Blocks of equations	79	19*	6	54
Blocks of variables	21	7	6	17
Discrete variables	21	21	0	0
* Excluding one equation for a dummy objective function				

The argument for using simultaneous optimization is that the resources and time required is greatly reduced, because the high sensitivity between the two design problems requires a wide search space resulting in a combinatorial explosion. This sensitivity is illustrated in Figure 5 where three contours are plotted based on the decomposition results. In Figure 5 A the sensitivity of T_c , P_c and \dot{W}_{net} is shown and it can be deduced that there is no definite area where a specific combination of the two properties provide a high value of the objective function. On the contrary, the gradients indicate a high correlation that result in several scattered areas that have \dot{W}_{net} . The same is seen in Figure 5.B with ω and T_c and in Figure 5.C with P_c and ω . In Figure 5, the numbers closest to 1 or -1 have the strongest correlation and any element that is higher than 0.5 or lower than -0.5 is marked red. It can be seen that there is a high correlation between several variables. Such as the correlation between \dot{W}_{net} with UA_{boiler} (low), $UA_{condenser}$ (high) and $UA_{recuperator}$ (high), which matches with the observations made in the case study result of Figure 4. A correlation is also observed between the common variables and the process variables, such as T_c with UA_{boiler} and T_c with P_1 . Thus, a decomposed approach is a sub-optimal approach because the fluid properties cannot be correlated with the process performance, therefore requiring that all feasible fluids to be tested.

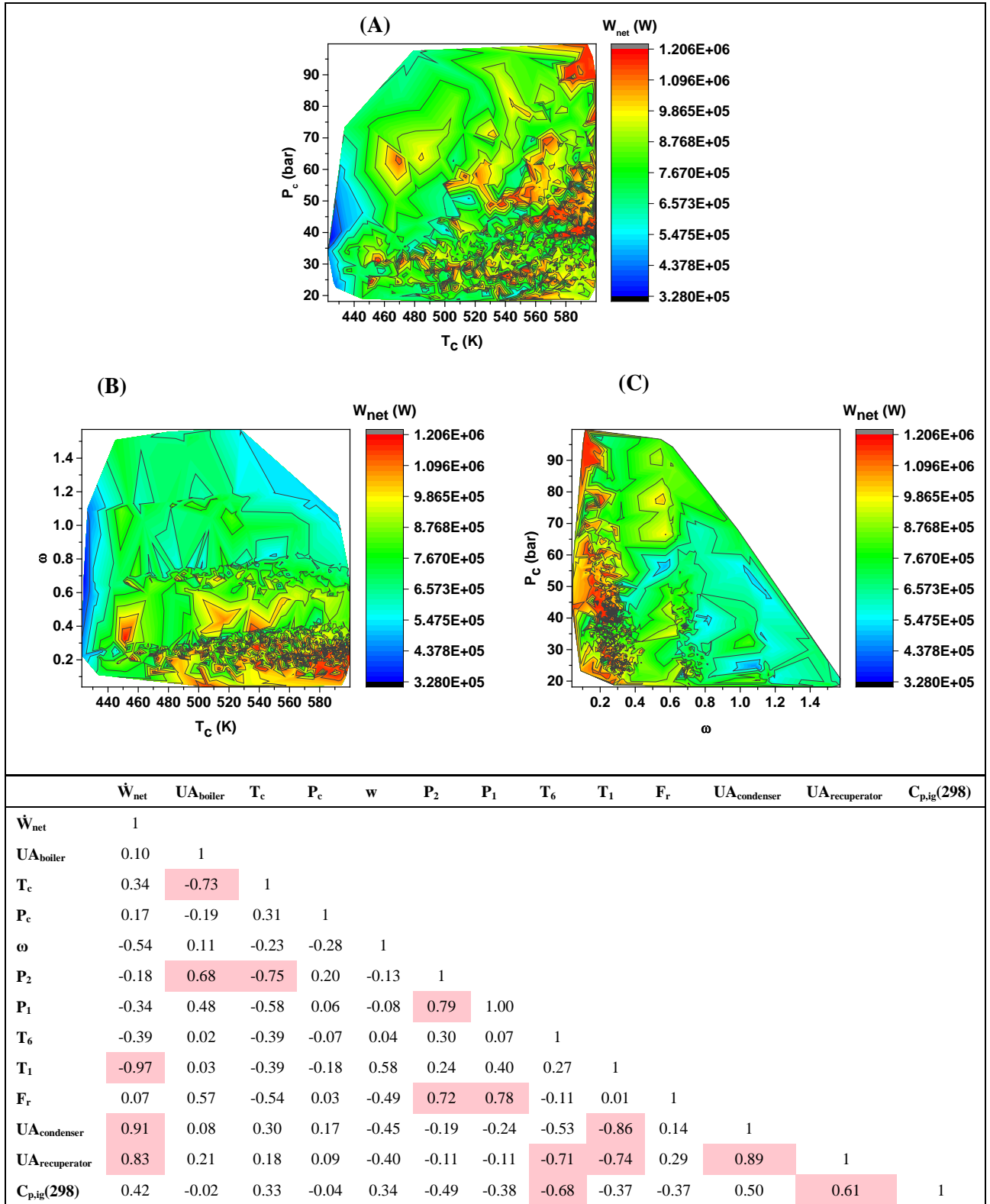


Figure 5: Cross-correlation for solution candidates obtained from the decomposed solution approach

3.2.2 Heuristic selection of fluids

Alternatives to the decomposition method also exist. For example, a heuristic selection of a set of known refrigerants is a common method. However, this inherently leads to a sub-optimal design route because of the limited availability of fluids (due to regulations) and due to the fact that no specific set of property values can give an indication of the process performance. In the following it is shown that a selection of the conventionally highest performing refrigerants does not perform as well as the design solution found in this paper.

The global optimal fluid (2,2,3,3,4,4,5,5-octafluorohexane) designed in the case study employing pinch point constraints was compared with conventional fluids used in similar ORC unit applications. The conventional fluids were selected from the scientific literature [33]. The fluids were compared on the basis of three selected process metrics: Net power output, pressure ratio and degree of superheating, where the reference value of unity is relative to the global optimal fluid designed in the present study. Net power output directly indicates the performance of the cycle. A high pressure ratio can have a negative influence on the expander performance and/or expander cost. The degree of superheating is related to the heat transfer area, and therefore by implication to investment cost, for the boiler, since the heat transfer performance of vapour superheating is poor. In the comparison (Figure 6), it can be seen that the generated fluid in this resulting from the current work outperforms the conventional fluids, but it also has one of the highest pressure ratios whilst keeping a low degree of superheating. However, it is worth noting that MM has more than a three-fold higher pressure ratio than the generated fluid. The low superheating is good since it means improved heat utilization and lower heat exchanger area requirements.

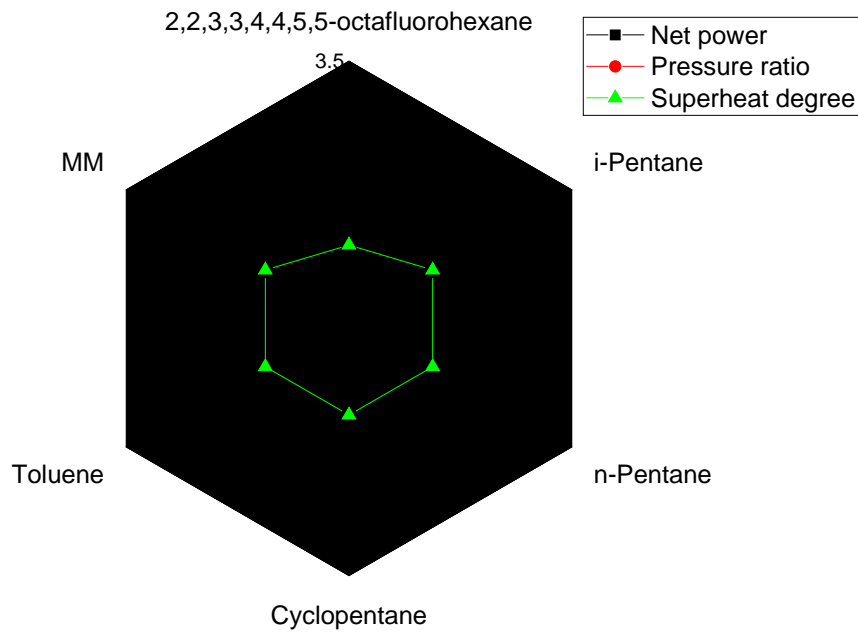


Figure 6: Optimal fluid comparison against benchmarks

3.2.3 Continuous-molecular targeting approach (CoMT-CAMD)

CoMT-CAMD methods are used when the combined product and process model is infeasible to solve simultaneously. In this way, the integer variables of molecular design are relaxed to obtain a continuous NLP that is easier to solve than the complete MINLP. Subsequently, molecules must be designed that have the same (or close to) relaxed molecular properties. However, since the simultaneous optimization of the fluid and cycle is possible in the case presented here, such approaches are not needed. Nevertheless, the information obtained from such a study is valuable, in that the optimal theoretical properties can be identified. In optimization, this is also termed a ‘relaxed’ solution. Additionally, the approach can give a good indication of the theoretical maximum objective function achievable, for a given problem. In this case, it provides an indication of how close the optimal solution from the simultaneous or decomposed solution approach is to the theoretical maximum. In order to illustrate this, a study was performed with the model and conditions presented in this paper. For the program this meant that the 21 discrete variables become free variables. This was solved and it was found that the maximum objective function was 1.6 MW, which as expected is higher than the result obtained by other methods. The product properties are given in Table 8.

Table 8: Relaxed fluid design properties with a CoMT-CAMD approach

	T_c (K)	P_c (bar)	ω (-)	W_{net} (MW)
Relaxed solution	469.77	37.81	1	1.6
Closest integer solution 1: 2 CH ₃ , 1 CH ₂ F, 1 CF, 1 CF ₂	462.22	33.69	0.70	0.7
Closest integer solution 2: 2 CH ₃ , 1 CH ₂ , 1CF, 1CHF ₂	468.24	30.84	0.72	0.6
Closest integer solution 3: 1 CH ₃ , 1 1CH ₂ =CH, 1 CF, 1 CHF ₂	469.69	31.89	0.70	0.6

The ideal gas heat capacity coefficients have no physical meaning and had to be fixed for a known fluid, here the optimal fluid from Table 5,. It is clear that the acentric factor has hit the upper bound. However, the marginal value reported by the solver is small (65 kW). This indicates that increasing the bound for the acentric factor would not improve the results significantly. From the databases used in this work, no fluid reported had an acentric factor higher than unity [7]. Using the CoMT-CAMD method, the task was then to find a pure fluid that matches those property values as closely as possible. With the product design MILP model used in this work (Eqs. (1)-(10) and in supplementary material Eqs. (1)-(12)), the closest integer solutions were found and are reported in Table 9. The search space was constrained to narrow down the search around the relaxed solution: T_c between 460 and 470 K, P_c between 28 and 48 bar and ω between 0.4 and 1. However, running the ORC process design optimization the designed fluid showed that the optimal objective function is 0.7 MW for integer solution 1. This is significantly lower than that given by the relaxed solution. The remaining two solutions gave 0.6 MW. This illustrates how important the values of the pure properties are, even though they cannot be clearly correlated with the process performance. Although more integer solutions close to the relaxed solution point could be investigated and optimized in the process, this study indicates that the simultaneous approach is preferred.

3.3 UA-optimization strategy

The high correlation between \dot{W}_{net} and $UA_{recuperator}$ and $UA_{condenser}$ with T_c and UA_{boiler} indicate that it would be favorable to employ a new optimization strategy for this case study result. Rather than basing the optimization on the lower bound for the pinch points in the heat exchangers to reduce the capital cost, an upper bound on

the UA values could be imposed instead. This would potentially address the issues with the high correlation. Furthermore, the designed optimal fluid is dependent on the process targets, in addition to the product targets. Thus, a pinch-point or UA-constrained method may yield different optimal fluids. In the current study this was demonstrated by employing UA constraints on the boiler and recuperator. The condenser was still modelled by considering a constant condensation temperature. The upper bounds were based on the pinch-point optimization results and were selected as 1.9×10^5 W/K and 2.6×10^5 W/K for the boiler and the recuperator, respectively. The decomposed approach was also used in this case and the results depicted in Figure 7. A similar profile is seen for the objective function, although now the upper bounds are reached for the UA constraints. This is now a comparable result for each fluid since the UA sizes are the same, with minor outliers. With this, a simultaneous solution strategy was used taking the new UA bounds. The results are summarized in Table 9. As shown, different results are now obtained, due to the inclusion of UA bounds, and a new fluid with a higher objective function than obtained previously observed.

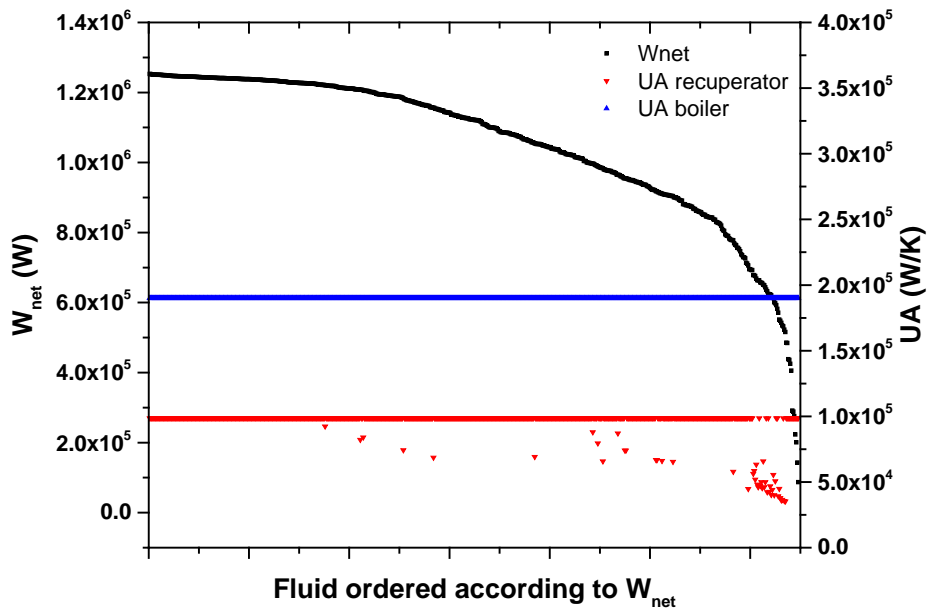
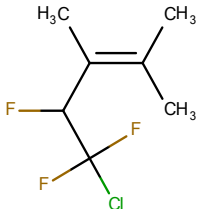
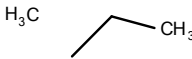
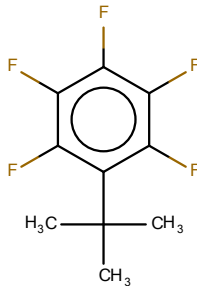


Figure 7: Decomposed optimization with UA-based strategy

Table 9: Simultaneous optimization results with UA value constraints. GWP and ODP are omitted, as they cannot be calculated with any of the generated groups.

Variable	Acyclic	Alicyclic	Aromatic
Structure			
n ₁	3 CH ₃ ; 1 C=C; 1 CHF; 1 CClF ₂	2 CH ₃ ; 1 CH ₂ ; 1 CH ₂ (cyc); 1 C(cyc); 1 CH=CH(cyc)	3 CH ₃ ; 1 aC-C; 5 aC-F
IUPAC	5-chloro-4,5,5-trifluoro-2,3-dimethylpent-2-ene	3-ethyl-3-methylcyclobut-1-ene	1-tert-butyl-2,3,4,5,6-pentafluorobenzene
q	1	0	0
\dot{W}_{net} (W)	1,253,071	1,256,810	936,343
T _c (K)	595.99	586.80	588.81
P _c (bar)	29.61	33.26	21.21
ω	0.188	33.261	0.467
C _{p,A}	-88.23	-137.77	-458.53
C _{p,B}	1.30	1.26	3.50
C _{p,C}	-1.36E-03	-1.37E-03	-5.02E-03
C _{p,D}	5.30E-07	9.56E-07	2.55E-06
P ₁ (bar)	0.05	0.06	0.05
P ₂ (bar)	3.64	3.89	2.23
T ₁ (K)	303.16	303.15	339.14
T _{2r} (K)	303.35	303.38	339.27
T ₃ (K)	408.15	408.15	408.15
T ₅ (K)	448.28	440.25	456.29
T ₆ (K)	477.77	483.70	461.29
T _{7r} (K)	428.14	429.96	425.09
T ₈ (K)	307.94	305.93	341.95
T _{g1} (K)	509.00	509.00	509.00
T _{g2} (K)	496.86	492.55	506.84
T _{g3} (K)	456.05	450.16	462.66
T _{g4} (K)	437.87	436.97	438.52
F _r (mol/s)	101.48	104.88	87.35
UA _{boiler} (W/K)	190,000	190,000	190,000
UA _{condenser} (W/K)	375,437	377,798	343,235
UA _{recuperator} (W/K)	270,000	270,000	270,000

3.4 SWOT analysis

The main contribution of the paper is the new simultaneous design method for the working fluid and organic Rankine cycle. Therefore, the method is now SWOT analyzed to further illustrate its benefits and limitations. The analysis is given in Table 10.

Table 10: SWOT analysis

Strengths	Weaknesses
<ul style="list-style-type: none">• Fluid and cycle can simultaneously be designed and optimized.• The design time is much lower compared to conventional methods.• The design solution in the case shown here was globally optimal, which would not have been possible with other methods.	<ul style="list-style-type: none">• The method requires a model for both the fluid design and the cycle process.• The problems need to be well bounded and a feasible initial point is needed.• The method is prone to uncertainties, as with any prediction method.
Opportunities	Threats
<ul style="list-style-type: none">• New types of fluids can be designed that otherwise would not have been selected by heuristics.• The fluids designed can either be completely novel or be available from other application areas.• More sustainable fluids can be designed that comply with international regulations.	<ul style="list-style-type: none">• The decomposed method can be preferred when all feasible fluid designed solutions are desired, e.g. for sensitivity studies.• Use of more complex and high fidelity thermodynamic models or process models can make the simultaneous solution of the MINLP infeasible.

4. Conclusions

The presented approach designed a working fluid and ORC unit that performs better than conventional fluids in terms of net power output and environmental properties with respect to global warming potential and ozone depletion potential. Furthermore, a relaxed design problem solution indicates that the problem bounds are reasonable and that the optimal solution is close to the theoretical maximum. The high sensitivity between fluid and cycle design variables experienced for state-of-the-art methods was overcome with the simultaneous approach presented and applied in this paper. Furthermore, the sensitivity is quantified and analyzed using a decomposition solution strategy where all feasible solutions were obtained. It was shown that this sensitivity could be addressed by employing a proposed UA-bound optimization strategy. The results suggest that the optimal fluid is 2,2,3,3,4,4,5,5-octafluorohexane (1.2 MW) using the simultaneous approach and fixed pinch points, and 5-chloro-4,5,5-trifluoro-2,3-dimethylpent-2-ene (1.25 MW) with the simultaneous approach and UA-bound optimization strategy. Thus, this paper presents an approach to overcome many challenges in fluid-cycle design and can likely be applied in other types of cycle as well.

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